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# GALVANO-THERMOMAGNETIC PHENOMENA AND THE FIGURE OF MERIT IN BISMUTH—I TRANSPORT PROPERTIES OF INTRINSIC MATERIAL

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**Abstract**—Transport theory based on the relaxation time formalism has been applied to bismuth; the results are used in Part II of this paper to determine the figure of merit of Bi in energy conversion processes. Using the Jones–Shoenberg model for bismuth, analytic expressions have been derived for the electrical resistivity, thermal conductivity, and for the Hall, Seebeck and Nernst coefficients. The Boltzmann transport equation was solved for the perturbed distribution function using anisotropic relaxation times. The result was then introduced in the transport integrals for the electric current and for energy flux to obtain the phenomenological equations for each set of charge carriers associated with a given ellipsoid. The contributions of each group of carriers were then added in the common symmetry coordinate system of the crystal to obtain the above-mentioned transport coefficients. To derive analytic expressions, it was necessary to consider the special cases where the magnetic field is aligned with each of the three symmetry axes and to pass to the limit of very low or very high magnetic fields.

## 1. PRELIMINARIES

RECENTLY considerable interest has developed in the application of the Nernst and Nernst–Ettingshausen effects to energy conversion; this, in turn, has stimulated a search for suitable device materials. Among the earliest experimental studies in this direction were measurements on the galvano-thermomagnetic properties, figure of merit, and general device performance of Bi and Bi–Sb alloys [1–4]. These experiments provide an opportunity for checking out numerical predictions based on transport theory; if the answers are in agreement with experiment, then the theory can be used in further investigations concerning optimal operating conditions of the device. The purpose of our work is thus two-fold. In Part I transport theory is developed in some detail to establish several new features; namely: (a) obtaining the solution of the Boltzmann transport equation for the very general case of anisotropic relaxation times, arbitrary magnetic field strengths, and temperature gradients, (b) deriving general thermodynamic relations for the over-all Seebeck and thermal conductivity tensors in terms of one-band contributions, (c) introducing anisotropic mobilities into the equations of interest, (d) establishing the necessary refinements of earlier transport theories [5, 6] which bring theory in accord with experiments, and (e) setting up all explicit formulae needed for later use. In Part II we check the theoretical predictions against available experimental data for Bi and then utilize the theory for calculating the appropriate figures of merit.

The band model which is used will be introduced in Section 3; however, it is well to remark here that we shall generalize the ABELES–MEIBOOM [5] treatment of Bi by taking into account the JONES–SHOENBERG band model refinement [7]. Also, from general considerations it emerges [8] that materials best suited for energy conversion processes

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based on the Nernst and Nernst–Ettingshausen effects are intrinsic; we therefore specialize to this case quite early. Other simplifications are introduced as needed to obtain the final results in tractable form.

We begin with the solution of the Boltzmann equation in the relaxation time formalism. The procedure parallels that of an earlier derivation [9] to which it reduces for the isotropic case. The reader is referred to this discussion for certain details and symbols.

One should note at the outset that the external force acting on charge carriers in a band in zero magnetic field is not simply the applied electric field **E**, but, more generally, the gradient of the band edge, $\nabla_{\mathbf{r}}\mathscr{E}_B$ [9]. With this modification, the Boltzmann transport equation for isotropic media reads:

$$(Ze/\hbar)[\nabla_{\mathbf{r}}(-\mathscr{E}_B/Ze) + (\mathbf{v} \times \mathbf{H})/c] \,.\, \nabla_{\mathbf{k}} f + \mathbf{v} \,.\, \nabla_{\mathbf{r}} f = -(f - f_0)\tau^{-1}, \tag{1.1}$$

where $Z = +1$ for holes and $-1$ for electrons, $\mathbf{v} \equiv (1/\hbar)\nabla_{\mathbf{k}}\mathscr{E}$, $\mathscr{E}$ and $\mathscr{E}_B$ are the energies and band edge energies, $f$ or $f_0$ are the actual or equilibrium distribution functions and $\tau$ is the relaxation time; the remaining symbols have their conventional significance. We obtain an approximate solution to equation (1.1) by the usual method [10] of setting $f = f_0$ for first and third terms on the left and $f = f_0 - \mathbf{v} \,.\, \mathbf{\Psi}(\partial f_0/\partial \varepsilon)$ in the remainder. The first objective in the general derivation is to find an expression for the quantity $\mathbf{\Psi}$. For this purpose, one proceeds essentially as in [9]. The only modification required to adapt the result to anisotropic media consists in the replacement of $\tau^{-1}$ by the tensor $\overleftrightarrow{\tau}^{-1} \equiv \overleftrightarrow{\nu}$. The generalization of equation (1.8), [9], is thus given as:

$$\mathbf{P} \,.\, \mathbf{v} - (Ze/\hbar c)(\mathbf{v} \times \mathbf{H}) \,.\, (\mathbf{\Psi} \,.\, \nabla_{\mathbf{k}}\mathbf{v}) = (\overleftrightarrow{\tau}^{-1} \,.\, \mathbf{\Psi}) \,.\, \mathbf{v}, \tag{1.2}$$

where

$$\mathbf{P} \equiv Ze\nabla_{\mathbf{r}}(\mathscr{E}_B/e) - T\nabla_{\mathbf{r}}(\mu_B/T) - (\varepsilon/T)\nabla_{\mathbf{r}}T \tag{1.3a}$$

$$\equiv Ze\nabla_{\mathbf{r}}(\zeta/e) + [(\mu_B - \varepsilon)/T]\nabla_{\mathbf{r}}T. \tag{1.3b}$$

In the above, $\mu_B \equiv \zeta - \mathscr{E}_B$, and $\varepsilon \equiv \mathscr{E} - \mathscr{E}_B$, where $\zeta$ is the Fermi level.

In the principal coordinate system of a particular ellipsoid, one can write

$$\nabla_{\mathbf{k}} v/\hbar = \nabla_{\mathbf{k}'}\nabla_{\mathbf{k}'}\varepsilon/\hbar^2,$$

where the primed coordinates serve as a reminder that this special coordinate system is being used; the quantity on the right represents a diagonal entry of the reciprocal mass tensor $\overleftrightarrow{\mathbf{q}} \equiv \overleftrightarrow{\mathbf{m}}^{-1}$. On inserting this result in equation (1.2) and applying the triple scalar product rule to the term $(\mathbf{v} \times \mathbf{H}) \,.\, (\mathbf{\Psi} \,.\, \overleftrightarrow{\mathbf{q}})$, one obtains:

$$\{\mathbf{P} - (Ze/c)[\mathbf{H} \times (\mathbf{\Psi} \,.\, \overleftrightarrow{\mathbf{q}})] - (\overleftrightarrow{\tau}^{-1} \,.\, \mathbf{\Psi})\} \,.\, \mathbf{v} = 0. \tag{1.4}$$

As has been discussed in connection with the comparable equation, (1.11b) of [9], equation (1.4) can only be satisfied by requiring that the quantity in curly braces vanish. In addition, we introduce a new variable $\mathbf{\Psi}^*$, defined as $\mathbf{\Psi} \equiv \overleftrightarrow{\tau} \,.\, \mathbf{\Psi}^*$. Equation (1.4) can then be rearranged to read:

$$\mathbf{\Psi}^* - (Ze/c)[(\overleftrightarrow{\tau} \,.\, \mathbf{\Psi}^*) \,.\, \overleftrightarrow{\mathbf{q}}] \times \mathbf{H} = \mathbf{P}. \tag{1.5}$$

To solve the above, we operate with $\overleftrightarrow{\tau}.$ on the left; this is to be followed with the operation $.\overleftrightarrow{q}$ from the right and finally, by the operation $\times\mathbf{H}$ from the right. One then obtains:

$$[(\overleftrightarrow{\tau}.\mathbf{\Psi}^*).\overleftrightarrow{q}]\times\mathbf{H}-(Ze/c)\left\{\left[\overleftrightarrow{\tau}.\{[(\overleftrightarrow{\tau}.\mathbf{\Psi}^*).\overleftrightarrow{q}]\times\mathbf{H}\}\right].\overleftrightarrow{q}\right\}\times\mathbf{H}=[(\overleftrightarrow{\tau}.\mathbf{P}).\overleftrightarrow{q}]\times\mathbf{H}. \quad (1.6)$$

The next step consists in evaluating the quantity sandwiched between $Ze/c$ and $\times\mathbf{H}$ in the second term of equation (1.6). The relaxation time formulation of the Boltzmann transport theory rests on the assumption that energies are conserved in the collision between charge carriers, and that the velocity is randomized during such encounters. Also, consistent with the above assumption, scattering of carriers from one valley to another is assumed to be included in the relaxation time $\tau$. HERRING and VOGT [11] have shown that in these circumstances $\overleftrightarrow{\tau}$ is a diagonal tensor in the ellipsoidal coordinate system. Let us set:

$$\overleftrightarrow{\tau}=\begin{bmatrix}\tau_{x'} & 0 & 0\\ 0 & \tau_{y'} & 0\\ 0 & 0 & \tau_{z'}\end{bmatrix};\quad \overleftrightarrow{q}=\begin{bmatrix}\frac{1}{m_{x'}} & 0 & 0\\ 0 & \frac{1}{m_{y'}} & 0\\ 0 & 0 & \frac{1}{m_{z'}}\end{bmatrix};\quad \begin{array}{l}\mathbf{H}=(H_{x'},H_{y'},H_{z'}).\\ \mathbf{\Psi}^*=(\Psi^*_{x'},\Psi^*_{y'},\Psi^*_{z'})\end{array} \quad (1.7)$$

On performing the indicated operations in the term under consideration, one arrives at the following result:

$$[\![\overleftrightarrow{\tau}.\{[(\overleftrightarrow{\tau}.\mathbf{\Psi}^*).\overleftrightarrow{q}]\times\mathbf{H}\}]\!].\overleftrightarrow{q}=\mathbf{\Psi}^*\times(\overleftrightarrow{\mathbf{C}}.\mathbf{H}), \quad (1.8a)$$

where

$$\overleftrightarrow{\mathbf{C}}\equiv\overleftrightarrow{\mathbf{m}}:\overleftrightarrow{\tau}^{-1}/\|\overleftrightarrow{\mathbf{m}}\|\,\|\overleftrightarrow{\tau}^{-1}\|, \quad (1.8b)$$

in which $\|\overleftrightarrow{\mathbf{m}}\|$ is the determinant of the mass tensor. Equation (1.8) may be checked by substituting from equation (1.7) on both sides, thus obtaining an identity. We now substitute equation (1.8) into equation (1.6) and apply the triple vector product rule to the resulting middle term, $(Ze/c)[\mathbf{\Psi}^*\times(\mathbf{C}.\mathbf{H})]\times\mathbf{H}$, to obtain:

$$[(\overleftrightarrow{\tau}.\mathbf{\Psi}^*).\overleftrightarrow{q}]\times\mathbf{H}-(Ze/c)\{(\mathbf{H}.\mathbf{\Psi}^*)(\overleftrightarrow{\mathbf{C}}.\mathbf{H})-[\mathbf{H}.(\overleftrightarrow{\mathbf{C}}.\mathbf{H})]\mathbf{\Psi}^*\}=[(\overleftrightarrow{\tau}.\mathbf{P}).\overleftrightarrow{q}]\times\mathbf{H}. \quad (1.9)$$

Next, return to equation (1.5) and operate on both sides with $.\mathbf{H}(\overleftrightarrow{\mathbf{C}}.\mathbf{H})$ from the right. By the triple scalar product rule, the resulting second term on the left vanishes identically, leaving:

$$(\mathbf{\Psi}^*.\mathbf{H})(\overleftrightarrow{\mathbf{C}}.\mathbf{H})=(\mathbf{P}.\mathbf{H})(\overleftrightarrow{\mathbf{C}}.\mathbf{H}), \quad (1.10)$$

so that on substituting this result into equation (1.9), we finally obtain:

$$[(\overleftrightarrow{\tau}.\mathbf{\Psi}^*).\overleftrightarrow{q}]\times\mathbf{H}=(Ze/c)(\mathbf{P}.\mathbf{H})(\overleftrightarrow{\mathbf{C}}.\mathbf{H})-(Ze/c)[\mathbf{H}.(\overleftrightarrow{\mathbf{C}}.\mathbf{H})]\mathbf{\Psi}^*+[(\overleftrightarrow{\tau}.\mathbf{P}).\overleftrightarrow{q}]\times\mathbf{H}. \quad (1.11)$$

We have hereby succeeded in reformulating the second term of equation (1.5) in a manner that allows this relation to be solved for $\mathbf{\Psi}^*$. Inserting equation (1.11), one obtains:

$$\mathbf{\Psi}\equiv\overleftrightarrow{\tau}.\mathbf{\Psi}^*=\frac{\overleftrightarrow{\tau}.\{\mathbf{P}+(e/c)^2(\mathbf{P}.\mathbf{H})(\overleftrightarrow{\mathbf{C}}.\mathbf{H})+(Ze/c)[(\overleftrightarrow{\tau}.\mathbf{P}).\overleftrightarrow{q}]\times\mathbf{H}\}}{1+(e/c)^2[\mathbf{H}.(\overleftrightarrow{\mathbf{C}}.\mathbf{H})]} \quad (1.12)$$

from which the distribution function $f$ can be calculated. If the relaxation time is a scalar, if $\nabla_r T = 0$, and for homogeneous materials where $\nabla_r(\mathscr{E}_B/Ze) = \mathbf{E}$ when $\nabla_r T = 0$, the above reduces to the relation cited by Shibuya [12] and extended to anisotropic relaxation times by Bullis [13].

## 2. THE GENERAL PHENOMENOLOGICAL EQUATIONS

The second task consists of writing down the phenomenological equations, based on the transport of electric charge and of "kinetic energy" $\varepsilon$, as given by:

$$\mathbf{J} = (Ze/4\pi^3)\int \mathbf{v}f\, \mathrm{d}^3\mathbf{k} = -(Ze/4\pi^3)\int \mathbf{v}(\mathbf{v}\,.\,\mathbf{\Psi})(\partial f_0/\partial\varepsilon)\, \mathrm{d}^3\mathbf{k} \tag{2.1a}$$

$$\mathbf{J}_{Q'} = (1/4\pi^3)\int \varepsilon\mathbf{v}f\, \mathrm{d}^3\mathbf{k} = -(1/4\pi^3)\int \varepsilon\mathbf{v}(\mathbf{v}\,.\,\mathbf{\Psi})(\partial f_0/\partial\varepsilon)\, \mathrm{d}^3\mathbf{k}. \tag{2.1b}$$

In the above, the integral involving $f_0$ vanishes identically. To obtain an explicit formulation, we substitute for $\mathbf{\Psi}$ from equation (1.12), utilizing equations (1.3b), (1.7) and (1.8b). After carrying out the required operations, one obtains the following expression for the $x'$ component of $\mathbf{\Psi}$:

$$\begin{aligned}
\Psi_{x'}\Delta' &= \tau_{x'}P_{x'} + (Ze/c)^2\tau_{x'}\tau_{y'}\tau_{z'}(H_{x'}/m_{y'}m_{z'})(H_{x'}P_{x'} + H_{y'}P_{y'} + H_{z'}P_{z'}) - \\
&\quad - (Ze/c)(\tau_{x'}\tau_{z'}H_{y'}P_{z'}/m_{z'} - \tau_{x'}\tau_{y'}H_{z'}P_{y'}/m_{y'}) \\
&= [Ze\tau_{x'} + (Ze^3/c^2)(\tau_{x'}\tau_{y'}\tau_{z'}H_{x'}^2/m_{z'}m_{y'})]\nabla_{x'}(\zeta/e) + \\
&\quad + [(Ze^3/c^2)(\tau_{x'}\tau_{y'}\tau_{z'}H_{x'}H_{y'}/m_{y'}m_{z'}) + (e^2/c)(\tau_{x'}\tau_{y'}H_{z'}/m_{y'})]\nabla_{y'}(\zeta/e) + \\
&\quad + [(Ze^3/c^2)(\tau_{x'}\tau_{y'}\tau_{z'}H_{z'}H_{x'}/m_{y'}m_{z'}) - (e^2/c)(\tau_{x'}\tau_{z'}H_{y'}/m_{z'})]\nabla_{z'}(\zeta/e) + \\
&\quad + [(\mu_B - \varepsilon)/T]\tau_{x'}[1 + (e^2/c^2)(\tau_{y'}\tau_{z'}H_{x'}^2/m_{y'}m_{z'})]\nabla_{x'}T + \\
&\quad + [(\mu_B - \varepsilon)/T](\tau_{x'}\tau_{y'}/m_{y'})[(Ze/c)H_{z'} + (e^2/c^2)(\tau_{z'}H_{x'}H_{y'}/m_{z'})]\nabla_{y'}T + \\
&\quad + [(\mu_B - \varepsilon)/T](\tau_{x'}\tau_{z'}/m_{z'})[(-Ze/c)H_{y'} + (e^2/c^2)(\tau_{y'}H_{x'}H_{z'}/m_{y'})]\nabla_{z'}T,
\end{aligned} \tag{2.2}$$

where

$$\Delta' \equiv 1 + (e^2/c^2)[\tau_{y'}\tau_{z'}H_{x'}^2/m_{y'}m_{z'} + \tau_{x'}\tau_{z'}H_{y'}^2/m_{x'}m_{z'} + \tau_{x'}\tau_{y'}H_{z'}^2/m_{x'}m_{y'}]. \tag{2.3}$$

Corresponding relations for $\Psi_{y'}$ and $\Psi_{z'}$ are obtained by cyclic permutation of the component subscript.

Equation (2.2) and its $y', z'$ analogues must now be substituted in equation (2.1). In this connection, it becomes convenient to introduce the following transport integrals ($\lambda', \nu' = x', y', z'$):

$$K_k^{(\lambda'\lambda')} \equiv -\frac{1}{4\pi^3}\iiint \frac{v_{\lambda'}^2\tau_{\lambda'}\varepsilon^{k-1}}{\Delta'}\frac{\partial f_0}{\partial\varepsilon}\,\mathrm{d}^3\mathbf{k} \tag{2.4a}$$

$$G_g^{(\lambda'\nu')} \equiv -\frac{1}{4\pi^3 c}\iiint \frac{v_{\lambda'}^2\tau_{\lambda'}\tau_{\nu'}\varepsilon^{g-1}}{m_{\nu'}\Delta'}\frac{\partial f_0}{\partial\varepsilon}\,\mathrm{d}^3\mathbf{k} \tag{2.4b}$$

$$L_l^{(\lambda'\lambda')} \equiv -\frac{1}{4\pi^3 c^2}\iiint \frac{m_{\lambda'}v_{\lambda'}^2\tau_{x'}\tau_{y'}\tau_{z'}\varepsilon^{l-1}}{m_{x'}m_{y'}m_{z'}\Delta'}\frac{\partial f_0}{\partial\varepsilon}\,\mathrm{d}^3\mathbf{k}. \tag{2.4c}$$

It is expedient to reformulate these integrals by expressing the energy $\varepsilon$ of charge carriers relative to the appropriate band edge as:

$$\varepsilon = (\hbar^2/2)(k_{x'}^2/m_{x'} + k_{y'}^2/m_{y'} + k_{z'}^2/m_{z'}) \tag{2.5}$$

in the principal coordinate system of an ellipsoid. We can then introduce a new variable, $\xi_{\lambda'} = k_{\lambda'}^2/m_{\lambda'}$, with which (2.5) may be rewritten as:

$$\varepsilon = (\hbar^2/2)\sum_{\lambda'} \xi_{\lambda'}^2 = \hbar^2\xi^2/2. \tag{2.6}$$

The above equation characterizes a set of concentric spheres in $\boldsymbol{\xi}$-space. Henceforth, we assume that the $\tau_{\lambda'}$ are functions of $\varepsilon$ only. In this event, we may write $d^3\boldsymbol{\xi} = 4\pi\xi^2\,d\xi$, whence:

$$d^3\mathbf{k} = (m_{x'}m_{y'}m_{z'})^{1/2}\,d^3\boldsymbol{\xi} = (4\pi/\hbar^3)(2\varepsilon)^{1/2}(m_{x'}m_{y'}m_{z'})^{1/2}\,d\varepsilon. \tag{2.7}$$

By spherical symmetry, $\xi_{\lambda'}^2 = (1/3)\xi^2$, then:

$$(m_{\lambda'}/\hbar^2)(\partial\varepsilon/\partial k_{\lambda'})^2 \equiv m_{\lambda'}v_{\lambda'}^2 = 2\varepsilon/3. \tag{2.8}$$

We now use equations (2.7) and (2.8) to rewrite (2.4) as:

$$K_k^{(\lambda')} = -\frac{2\sqrt{2}(m_{x'}m_{y'}m_{z'})^{1/2}}{3\pi^2 m_{\lambda'}\hbar^3}\int_0^\infty \frac{\tau_{\lambda'}\varepsilon^{k+1/2}}{\Delta'}\frac{\partial f_0}{\partial\varepsilon}\,d\varepsilon \tag{2.9a}$$

$$G_g^{(\lambda'v')} = -\frac{2\sqrt{2}(m_{x'}m_{y'}m_{z'})^{1/2}}{3\pi^2 c m_{\lambda'}m_{v'}\hbar^3}\int_0^\infty \frac{\tau_{\lambda'}\tau_{v'}\varepsilon^{g+1/2}}{\Delta'}\frac{\partial f_0}{\partial\varepsilon}\,d\varepsilon \tag{2.9b}$$

$$L_l = -\frac{2\sqrt{2}}{3\pi^2 c^2(m_{x'}m_{y'}m_{z'})^{1/2}\hbar^3}\int_0^\infty \frac{\tau_{x'}\tau_{y'}\tau_{z'}\varepsilon^{l+1/2}}{\Delta'}\frac{\partial f_0}{\partial\varepsilon}\,d\varepsilon. \tag{2.9c}$$

Utilizing either equations (2.4) or (2.9), the $x'$ component of the current density vector $J^{x'} = -(Ze/4\pi^3)\iiint v_{x'}^2\Psi_{x'}(\partial f_0/\partial\varepsilon)\,d^3\mathbf{k}$ becomes:

$$\begin{aligned}J^{x'} = {} & Ze(ZeK_1^{(x')} + Ze^3L_1H_{x'}^2)\nabla_{x'}(\zeta/e) + Ze(e^2G_1^{(x'y')}H_{z'} + Ze^3L_1H_xH_y)\nabla_{y'}(\zeta/e) + \\ & + Ze(-e^2H_{y'}G_1^{(x'z')} + Ze^3L_1H_{x'}H_{z'})\nabla_{z'}(\zeta/e) + (Ze/T)[(K_1^{(x')}\mu_B - K_2^{(x')}) + \\ & \qquad + e^2H_{x'}^2(L_1\mu_B - L_2)]\nabla_{x'}T \\ & + (e^2/T)[H_{z'}(G_1^{(x'y')}\mu_B - G_2^{(x'y')}) + ZeH_{x'}H_{y'}(L_1\mu_B - L_2)]\nabla_{y'}T + \\ & + (e^2/T)[-H_{y'}(G_1^{(x'z')}\mu_B - G_2^{(x'z')}) + ZeH_{x'}H_{z'}(L_1\mu_B - L_2)]\nabla_{z'}T.\end{aligned} \tag{2.10}$$

The corresponding quantities $J^{y'}$ and $J^{z'}$ are obtained by cyclic permutation of the coordinate indices. Furthermore, one can show that $J_{Q'}^{x'} = -(1/4\pi^3)\iiint \varepsilon v_{x'}^2\Psi_{x'}(\partial f_0/\partial\varepsilon)\,d^3\mathbf{k}$ is specified by a relation like equation (2.10), except that one power of $Ze$ is deleted from the right and that the subscripts $g$, $k$, and $l$ in equation (2.9) are raised by one unit. The remaining components are again found by permutation of coordinate indices.

The information discussed above can be succinctly summarized by the following relationship:

$$\left[\begin{array}{c}\mathbf{J}\\ \hline \mathbf{J}_{Q'}\end{array}\right] = \left[\begin{array}{c|c}\overleftrightarrow{\sigma} & \overleftrightarrow{\mathfrak{S}}\\ \hline \overleftrightarrow{\mathbf{U}} & \overleftrightarrow{\mathbf{Y}}\end{array}\right]\left[\begin{array}{c}\nabla(\zeta/e)\\ \hline \nabla T\end{array}\right], \tag{2.11a}$$

where in the principal coordinate system of each ellipsoid:

$$\overleftrightarrow{\sigma} = \begin{bmatrix} e^2K_1^{(x')} + e^4L_1H_{x'}^2 & Ze^3G_1^{(x'y')}H_{z'} + e^4L_1H_{x'}H_{y'} & -Ze^3G_1^{(x'z')}H_{y'} + e^4L_1H_{x'}H_{z'} \\ -Ze^3G_1^{(x'y')}H_{z'} + e^4L_1H_{x'}H_{y'} & e^2K_1^{(y')} + e^4L_1H_{y'}^2 & Ze^3G_1^{(y'z')}H_{x'} + e^4L_1H_{y'}H_{z'} \\ Ze^3G_1^{(x'z')}H_{y'} + e^4L_1H_{x'}H_{z'} & -Ze^3G_1^{(y'z')}H_{x'} + e^4L_1H_{y'}H_{z'} & + e^2K_1^{(z')} + e^4L_1H_{z'}^2 \end{bmatrix}; \tag{2.11b}$$

$$\overleftrightarrow{\mathfrak{S}} = \begin{bmatrix} (Ze/T)(K_1^{(x')}\mu_B - K_2^{(x')}) + (Ze^3/T)(L_1\mu_B - L_2)H_{x'}^2 & +(e^2/T)(G_1^{(x'y')}\mu_B - G_2^{(x'y')})H_{z'} + (Ze^3/T)(L_1\mu_B - L_2)H_{x'}H_{y'} & (-e^2/T)(G_1^{(x'z')}\mu_B - G_2^{(x'z')})H_{y'} + (Ze^3/T)(L_1\mu_B - L_2)H_{x'}H_{z'} \\ -(e^2/T)(G_1^{(x'y')}\mu_B - G_2^{(x'y')})H_{z'} + (Ze^3/T)(L_1\mu_B - L_2)H_{x'}H_{y'} & (Ze/T)(K_1^{(y')}\mu_B - K_2^{(y')}) + (Ze^3/T)(L_1\mu_B - L_2)H_{y'}^2 & (e^2/T)(G_1^{(y'z')}\mu_B - G_2^{(y'z')})H_{x'} + (Ze^3/T)(L_1\mu_B - L_2)H_{y'}H_{z'} \\ +(e^2/T)(G_1^{(x'z')}\mu_B - G_2^{(x'z')})H_{y'} + (Ze^3/T)(L_1\mu_B - L_2)H_{x'}H_{z'} & -(e^2/T)(G_1^{(y'z')}\mu_B - G_2^{(y'z')})H_{x'} + (Ze^3/T)(L_1\mu_B - L_2)H_{y'}H_{z'} & +(Ze/T)(K_1^{(z')}\mu_B - K_2^{(z')}) + (Ze^3/T)(L_1\mu_B - L_2)H_{z'}^2 \end{bmatrix}; \tag{2.11c}$$

$$\overleftrightarrow{U} = \begin{bmatrix} ZeK_2^{(x')} + Ze^3L_2H_{x'}^2 & e^2G_2^{(x'y')}H_{z'} + Ze^3L_2H_{x'}H_{y'} & -e^2G_2^{(x'z')}H_{y'} + Ze^3L_2H_{x'}H_{z'} \\ -e^2G_2^{(x'y')}H_{z'} + Ze^3L_2H_{x'}H_{y'} & ZeK_2^{(y')} + Ze^3L_2H_{y'}^2 & e^2G_2^{(y'z')}H_{x'} + Ze^3L_2H_{y'}H_{z'} \\ e^2G_2^{(x'z')}H_{y'} + Ze^3L_2H_{x'}H_{z'} & -e^2G_2^{(y'z')}H_{x'} + Ze^3L_2H_{y'}H_{z'} & ZeK_2^{(z')} + Ze^3L_2H_{z'}^2 \end{bmatrix}; \tag{2.11d}$$

and

$$\overleftrightarrow{Y} = \begin{bmatrix} (1/T)(K_2^{(x')}\mu_B - K_3^{(x')}) + (e^2/T)(L_2\mu_B - L_3)H_{x'}^2 & (Ze/T)(G_2^{(x'y')}\mu_B - G_3^{(x'y')})H_{z'} + (e^2/T)(L_2\mu_B - L_3)H_{x'}H_{y'} & -(Ze/T)(G_2^{(x'z')}\mu_B - G_3^{(x'z')})H_{y'} + (e^2/T)(L_2\mu_B - L_3)H_{x'}H_{z'} \\ (-Ze/T)(G_2^{(x'y')}\mu_B - G_3^{(x'y')})H_{z'} + (e^2/T)(L_2\mu_B - L_3)H_{x'}H_{y'} & (1/T)(K_2^{(y')}\mu_B - K_3^{(y')}) + (e^2/T)(L_2\mu_B - L_3)H_{y'}^2 & (Ze/T)(G_2^{(y'z')}\mu_B - G_3^{(y'z')})H_{x'} + (e^2/T)(L_2\mu_B - L_3)H_{y'}H_{z'} \\ (Ze/T)(G_2^{(x'z')}\mu_B - G_3^{(x'z')})H_{y'} + (e^2/T)(L_2\mu_B - L_3)H_{x'}H_{z'} & -(Ze/T)(G_2^{(y'z')}\mu_B - G_3^{(y'z')})H_{x'} + (e^2/T)(L_2\mu_B - L_3)H_{y'}H_{z'} & (1/T)(K_2^{(z')}\mu_B - K_3^{(z')}) + (e^2/T)(L_2\mu_B - L_3)H_{z'}^2 \end{bmatrix}. \tag{2.11e}$$

To avoid the complexities inherent in the use of equation (2.11), we now make another in a series of approximations by taking each $\tau_{\lambda'}$ to be independent of $\varepsilon$. In this event, we can rewrite equation (2.9a–c) as:

$$K_k^{(\lambda')} = (\tau_{\lambda'}/m_{\lambda'}\Delta')S_k \tag{2.12a}$$

$$G_g^{(\lambda'v')} = (\tau_{\lambda'}\tau_{v'}/m_{\lambda'}m_{v'}\Delta'c)S_g \tag{2.12b}$$

$$L_l = (\tau_{x'}\tau_{y'}\tau_{z'}/m_{x'}m_{y'}m_{z'}\Delta'c^2)S_l, \tag{2.12c}$$

in which a new transport integral

$$S_n = -\frac{2\sqrt{2}}{3\pi^2}\frac{(m_{x'}m_{y'}m_{z'})^{1/2}}{\hbar^3}\int_0^\infty \varepsilon^{n+1/2}\frac{\partial f_0}{\partial \varepsilon}\,\mathrm{d}\varepsilon \tag{2.13}$$

has been introduced; $n$ refers to the index $k, g, l$ in equation (2.12). The quantity $\Delta'$ is given by equation (2.3).

The zero magnetic field charge carrier conductivity partial mobility components are

$$u_{\lambda'} = e\tau_{\lambda'}/m_{\lambda'} \tag{2.14}$$

in the principal coordinate system of each ellipsoid. This relation applies since we assumed earlier that $\tau_{\lambda'}$ does not depend on $\varepsilon$; moreover, the $u_{\lambda'}$ represent mobilities in zero magnetic field. Equation (2.3) now becomes:

$$\Delta' = 1 + u_{y'}u_{z'}H_{x'}^2/c^2 + u_{x'}u_{z'}H_{y'}^2/c^2 + u_{x'}u_{y'}H_{z'}^2/c^2, \tag{2.15}$$

and the matrices (2.11) reduce to:

$$\overleftrightarrow{\sigma} = S_1 e\overleftrightarrow{\mathbf{M}} \tag{2.16a}$$

$$\overleftrightarrow{\mathfrak{S}} = ZQ_1\overleftrightarrow{\mathbf{M}}/T \tag{2.16b}$$

$$\overleftrightarrow{\mathbf{U}} = ZS_2\overleftrightarrow{\mathbf{M}} \tag{2.16c}$$

$$\overleftrightarrow{\mathbf{Y}} = Q_2\overleftrightarrow{\mathbf{M}}/eT, \tag{2.16d}$$

where $Q_i \equiv S_i\mu_B - S_{i+1}$, and where

$$\overleftrightarrow{\mathbf{M}} \equiv \frac{1}{\Delta'}\begin{bmatrix} u_{x'}\left[1 + u_{y'}u_{z'}\left(\frac{H_{x'}}{c}\right)^2\right] & u_{x'}u_{y'}\left(Z\frac{H_{z'}}{c} + u_{z'}\frac{H_{x'}H_{y'}}{c^2}\right) & u_{x'}u_{z'}\left(-Z\frac{H_{y'}}{c} + u_{y'}\frac{H_{x'}H_{z'}}{c^2}\right) \\ u_{x'}u_{y'}\left(-Z\frac{H_{z'}}{c} + u_{z'}\frac{H_{x'}H_{y'}}{c^2}\right) & u_{y'}\left[1 + u_{x'}u_{z'}\left(\frac{H_{y'}}{c}\right)^2\right] & u_{y'}u_{z'}\left(Z\frac{H_{x'}}{c} + u_{x'}\frac{H_{y'}H_{z'}}{c^2}\right) \\ u_{x'}u_{z'}\left(Z\frac{H_{y'}}{c} + u_{y'}\frac{H_{x'}H_{z'}}{c^2}\right) & u_{y'}u_{z'}\left(-Z\frac{H_{x'}}{c} + u_{x'}\frac{H_{y'}H_{z'}}{c^2}\right) & u_{z'}\left[1 + u_{x'}u_{y'}\left(\frac{H_{z'}}{c}\right)^2\right] \end{bmatrix}. \tag{2.16e}$$

The above relations represent the end result of the statistical transport theory for a group of charge carriers associated with an ellipsoid, in terms of the principal coordinate system of that particular ellipsoid. We now wish to correlate the tensor entries with quantities that are experimentally determined. For this purpose, it is convenient to introduce phenomenological equations in partially inverted form [14], namely:

$$\begin{bmatrix} \nabla\zeta/e \\ T\mathbf{J}_S \end{bmatrix} = \begin{bmatrix} \overleftrightarrow{\rho} & \overleftrightarrow{\mathfrak{p}} \\ \overleftrightarrow{\Pi} & -\overleftrightarrow{\kappa} \end{bmatrix}\begin{bmatrix} \mathbf{J} \\ \nabla T \end{bmatrix}. \tag{2.17}$$

The entries in the above relations are essentially definitions. Thus, when $\nabla T = 0$, $\nabla\zeta/e$ and $\mathbf{J}$ are interconnected by the resistivity tensor, $\overleftrightarrow{\rho}$; when $\mathbf{J} = 0$, $\nabla\zeta/e$ and $\nabla T$ are related by the Seebeck tensor $\overleftrightarrow{\mathfrak{p}}$. Again, for $\mathbf{J} = 0$, $T\mathbf{J}_S$ is the heat flux (energy transfer past unit area in the absence of a net particle transfer), which is related to the temperature gradient by the negative thermal conductivity tensor, $-\overleftrightarrow{\kappa}$. Finally, for $\nabla T = 0$, the functional dependence of $T\mathbf{J}_S$ on $\mathbf{J}$ involves the Peltier tensor, $\overleftrightarrow{\Pi}$. It is worth noting that the entries in the latter are connected to the $\overleftrightarrow{\mathfrak{p}}$ entries by the Casimir–Onsager reciprocity condition $\Pi_{ij}(-\mathbf{H}) = T\mathfrak{p}_{ji}(\mathbf{H})$; furthermore, $\rho_{ij}(-\mathbf{H}) = \rho_{ji}(\mathbf{H})$, and $\kappa_{ij}(-\mathbf{H}) = \kappa_{ji}(\mathbf{H})$.

For the moment, we will continue to consider only the group of charge carriers associated with a given ellipsoid. In this event, the entries in equations (2.17) can be expressed in terms of those in equation (2.11a) or (2.16) as follows: By appropriate manipulation of the results in [15], it can be shown that:

$$T\mathbf{J}_S = \mathbf{J}_{Q'} - \kappa_L \nabla T - (\mu_B/Ze)\mathbf{J}. \tag{2.18a}$$

Actually, we wish to ignore the contribution of the lattice thermal conduction processes to $T\mathbf{J}_S$ and define a new quantity $T\mathbf{J}_{S'}$ by

$$T\mathbf{J}_{S'} \equiv \mathbf{J}_{Q'} - (\mu_B/Ze)\mathbf{J}. \tag{2.18b}$$

Applying equation (2.18b) to equation (2.16), we can then write:

$$\begin{bmatrix} \mathbf{J} \\ \\ T\mathbf{J}_{S'} + \dfrac{\mu_B}{Ze}\mathbf{J} \end{bmatrix} = \begin{bmatrix} S_1 e\overleftrightarrow{\mathbf{M}} & \dfrac{ZQ_1}{T}\overleftrightarrow{\mathbf{M}} \\ \\ ZS_2\overleftrightarrow{\mathbf{M}} & \dfrac{Q_2}{eT}\overleftrightarrow{\mathbf{M}} \end{bmatrix} \begin{bmatrix} \nabla\zeta/e \\ \\ \nabla T \end{bmatrix}. \qquad \begin{matrix}(2.19a)\\ \\ (2.19b)\end{matrix}$$

Now solve for $\nabla\zeta/e$ in terms of $\mathbf{J}$ and $\nabla T$ in equation (2.19a) and eliminate $\nabla\zeta/e$ from equation (2.19b); also replace the $Q_i$ by their definition. We then obtain:

$$\begin{bmatrix} \nabla\zeta/e \\ \\ T\mathbf{J}_S \end{bmatrix} = \begin{bmatrix} \dfrac{\overleftrightarrow{\mathbf{M}}^{-1}}{S_1 e} & \left(\dfrac{S_2}{S_1} - \mu_B\right)\dfrac{1}{ZeT} \\ \\ \left(\dfrac{S_2}{S_1} - \mu_B\right)\dfrac{1}{Ze} & -\left(\dfrac{S_3 S_1 - S_2^2}{S_1 eT}\right)\overleftrightarrow{\mathbf{M}} \end{bmatrix} \begin{bmatrix} \mathbf{J} \\ \\ \nabla T \end{bmatrix}. \tag{2.20}$$

Comparison between equations (2.20) and (2.17) then leads to the following identifications:

$$\overleftrightarrow{\rho}_p^{(\nu)} = \overleftrightarrow{\mathbf{M}}^{-1(\nu)}/S_1^{(\nu)}e, \tag{2.21a}$$

where it is clear from equation (2.13) that $S_1$ depends on the effective mass of the carriers under consideration; $S_1$ is therefore provided with the index $\nu$. For all ellipsoids lying within a given band, $S_1^{(\nu)}$ is the same; this is also true of the mobilities of carriers in a given band.

One can determine $\overleftrightarrow{\mathbf{M}}^{-1(\nu)}$ in equation (2.21a) from equation (2.16e) using the standard inversion procedure. This leads to the result:

$$\overleftrightarrow{\rho}_p^{(\nu)} = \frac{1}{S_1^{(\nu)}e} \begin{bmatrix} \dfrac{1}{u_{x'}^{(\nu)}} & -Z_\nu \dfrac{H_{z'}^{(\nu)}}{c} & Z_\nu \dfrac{H_{y'}^{(\nu)}}{c} \\ Z_\nu \dfrac{H_{z'}^{(\nu)}}{c} & \dfrac{1}{u_{y'}^{(\nu)}} & -Z_\nu \dfrac{H_{x'}^{(\nu)}}{c} \\ -Z_\nu \dfrac{H_{y'}^{(\nu)}}{c} & Z_\nu \dfrac{H_{x'}^{(\nu)}}{c} & \dfrac{1}{u_{z'}^{(\nu)}} \end{bmatrix}. \tag{2.21b}$$

From a comparison of equations (2.20) and (2.17), the general Seebeck tensor is found to be:

$$\overleftrightarrow{\mathfrak{p}}_p^{(v)} = -\frac{Q_1^{(v)}}{Z_v e T S_1^{(v)}}\begin{bmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{bmatrix} \equiv \frac{S_2^{(v)}/S_1^{(v)} - \mu_B^{(v)}}{Z_v e T}\mathbf{[1]} \equiv \mathfrak{p}^{(v)}\mathbf{[1]}. \tag{2.22}$$

In the present approximation, therefore, the Seebeck coefficient for a single valley is isotropic.

Finally, the electronic contribution to the thermal conductivity is:

$$\overleftrightarrow{\boldsymbol{\kappa}}_p^{\prime(v)} = \frac{S_1^{(v)}S_3^{(v)} - S_2^{(v)^2}}{eTS_1^{(v)}}\overleftrightarrow{\mathbf{M}}^{(v)} = \frac{S_1^{(v)}S_3^{(v)} - S_2^{(v)^2}}{e^2TS_1^{(v)2}}\overleftrightarrow{\boldsymbol{\sigma}}_p^{(v)}. \tag{2.23}$$

Since $\overleftrightarrow{\boldsymbol{\kappa}}_p^{\prime(v)}$ is proportional to $\overleftrightarrow{\boldsymbol{\sigma}}_p^{(v)}$, the Wiedemann–Franz law holds in the approximation scheme used here.

Having disposed of the one-group problem, it remains to find expressions for the totality of carriers in all different groups of relevance. In general, the physical properties of anisotropic materials are characterized in terms of several bands, one or more of which is of the multi-valley form. For the summation, we use as a guiding principle the fact that the individual fluxes are additive, whereas the gradients $\nabla T$ and $\nabla\zeta/e$ are the same for each group of carriers. Furthermore, one should recognize that equation (2.17) is a thermodynamic relation that takes no account of the details of conduction processes. Hence, the form of equation (2.17) remains unaltered for the totality of charge carriers; $\mathbf{J}$ and $\mathbf{J}_S$, then refer to the total flux vectors, and the tensor entries specify the appropriate physical properties of the material as a whole.

Let us then determine the total current density from equation (2.19) as:

$$\begin{aligned}\mathbf{J}^{(T)} &= \sum_v \mathbf{J}^{(v)} = \sum_v S_1^{(v)} e\overleftrightarrow{\mathbf{M}}^{(v)}\cdot\nabla\zeta/e + \sum_v (Z_v Q_1^{(v)}\overleftrightarrow{\mathbf{M}}^{(v)}/T)\cdot\nabla T\\ &= \Big(\sum_v \overleftrightarrow{\boldsymbol{\sigma}}^{(v)}\Big)\cdot\nabla\zeta/e - \Big(\sum_v \mathfrak{p}^{(v)}\overleftrightarrow{\boldsymbol{\sigma}}^{(v)}\Big)\cdot\nabla T,\end{aligned} \tag{2.24}$$

where equation (2.22) was used to arrive at the second line. Likewise, from equations (2.20–2.23), the total entropy flux (exclusive of the contribution of the lattice to the heat conduction) is found to be:

$$T\mathbf{J}_{S'}^{(T)} = T\sum_v \mathbf{J}_{S'}^{(v)} = T\sum_v \mathfrak{p}^{(v)}\mathbf{J}^{(v)} - \sum_v \overleftrightarrow{\boldsymbol{\kappa}}^{\prime(v)}\cdot\nabla T. \tag{2.25}$$

Now eliminate $\mathbf{J}^{(v)}$ in the above, using equation (2.19a); then:

$$T\mathbf{J}_{S'}^{(T)} = -\sum_v \overleftrightarrow{\boldsymbol{\kappa}}^{\prime(v)}\cdot\nabla T + \sum_v T\mathfrak{p}^{(v)}(\overleftrightarrow{\boldsymbol{\sigma}}^{(v)}\cdot\nabla\zeta/e - \mathfrak{p}^{(v)}\overleftrightarrow{\boldsymbol{\sigma}}^{(v)}\cdot\nabla T). \tag{2.26}$$

For $\nabla T = 0$, it follows from equation (2.24) that $\mathbf{J}^{(T)} = \sum_v \overleftrightarrow{\boldsymbol{\sigma}}^{(v)}\cdot\nabla\zeta/e$ whence the total conductivity and resistivity tensor is:

$$\overleftrightarrow{\boldsymbol{\sigma}} = \sum_v \overleftrightarrow{\boldsymbol{\sigma}}^{(v)};\; \overleftrightarrow{\boldsymbol{\rho}} = \Big(\sum_v \overleftrightarrow{\boldsymbol{\sigma}}^{(v)}\Big)^{-1}. \tag{2.27}$$

According to equation (2.24) [see also equation (2.17)], when $\mathbf{J}^{(T)} = 0$, the total Seebeck tensor is given by:

$$\overleftrightarrow{\mathfrak{p}} \equiv \nabla(\zeta/e)/\nabla T]_{\mathbf{J}}(T) = 0 = \overleftrightarrow{\boldsymbol{\rho}}.\Big(\sum_v \mathfrak{p}^{(v)}\overleftrightarrow{\boldsymbol{\sigma}}^{(v)}\Big). \tag{2.28}$$

Finally, the total thermal conductivity (exclusive of the contribution from the lattice) is found from equation (2.17) as $-T\mathbf{J}_{S'}^{(T)}/\nabla T$ when $\mathbf{J} = 0$. Using this latter condition, we can eliminate $\nabla\zeta/e$ between equations (2.24) and (2.26), thereby obtaining:

$$\overleftrightarrow{\kappa}' = \sum_{\nu} \overleftrightarrow{\kappa}'^{(\nu)} + T \sum_{\nu} (\mathfrak{p}^{(\nu)})^2 \overleftrightarrow{\sigma}^{(\nu)} - T\Big(\sum_{\nu} \mathfrak{p}^{(\nu)} \overleftrightarrow{\sigma}^{(\nu)}\Big) . \overleftrightarrow{\rho} . \Big(\sum_{\nu} \mathfrak{p}^{(\nu)} \overleftrightarrow{\sigma}^{(\nu)}\Big)$$

$$= \sum_{\nu} \overleftrightarrow{\kappa}'^{(\nu)} + T \sum_{\nu} (\mathfrak{p}^{(\nu)})^2 \overleftrightarrow{\sigma}^{(\nu)} - T\Big(\sum_{\nu} \mathfrak{p}^{(\nu)} \overleftrightarrow{\sigma}^{(\nu)}\Big) . \overleftrightarrow{\mathfrak{p}}. \tag{2.29}$$

Having shown how to determine $\overleftrightarrow{\sigma}, \overleftrightarrow{\rho}, \overleftrightarrow{\mathfrak{p}}$ and $\overleftrightarrow{\kappa}'$ from one-group contributions, we can now apply the above theory to the case of Bi. Due to severe mathematical complexities which arise, we shall not explicitly determine $\overleftrightarrow{\kappa}'$ according to equation (2.29); the reader will note, however, that this can be done in principle through a knowledge of $\mathfrak{p}^{(\nu)}$ and $\overleftrightarrow{\sigma}^{(\nu)}$, since the $\overleftrightarrow{\kappa}'^{(\nu)}$ occurring in equation (2.29) can be eliminated via the Wiedemann–Franz formulation, equation (2.23).

## 3. TRANSPORT TENSORS FOR THE CONDUCTION BAND OF BISMUTH: THE TILTING OPERATION

Having constructed in Section 2 tensors for various transport coefficients in the principal coordinate system of each ellipsoid, we now begin the task of deriving the corresponding quantities for Bi. For this purpose, it is necessary to consider its band structure.

In our further work, we shall specify the orientation of ellipsoids with reference to a crystal axis system in which the binary, bisectrix and trigonal axes constitute the $x$, $y$, and $z$ directions.

Abeles and Meiboom [5] (AM) assumed a conduction band exhibiting six whole or six half ellipsoids which lie along the threefold binary axes and hence are separated by 60° in the $x$–$y$ plane. They also postulated a valence band in which two half or two whole ellipsoids lie along the $z$-axis. The final formulae are independent of whether the bands are assumed to contain six or three and two or one ellipsoids respectively; we arbitrarily consider the case where the conduction band contains three ellipsoids (labelled $\nu = 1,2,3$) and the valence band, one ellipsoid (labelled $\nu = 4$). We also introduce the Jones–Shoenberg (JS) refinement [7], in which the conduction band ellipsoids are rotated about their respective binary axes in such a manner as to preserve a three-fold symmetry about the trigonal axis. Also, we extend the AM treatment to the Seebeck and Nernst tensors. In recent years, experimental evidence for two additional band model refinements have appeared in the literature; namely, (a) the non-parabolicity of the bands [16], and (b) the occurrence of additional bands [17]. We will neglect these latter complications because introduction of (a) in the theory generally leads to integrals which have to be evaluated numerically, and both (a) and (b) lead to extremely complicated expressions.

The first step in the derivation consists in introducing a similarity transformation which rotates each conduction band ellipsoid about the appropriate binary axis, (i.e., about its own $x'$ axis) by an angle $\theta(\sim -6°)$, thereby bringing its $x'$, $y'$ plane into proper alignment with the $x$, $y$ crystal plane. The transformation which accomplishes this will be denoted as the "tilting operation" and the conduction band ellipsoids which have been subjected to this operation are said to have been tilted (into the $xy$ plane). The tilting operation is specified by the tensor:

$$\overleftrightarrow{\mathfrak{B}}_\theta = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & \sin\theta \\ 0 & -\sin\theta & \cos\theta \end{bmatrix}. \tag{3.1}$$

To determine the effect of this tilting operation, it is simplest to begin with the resistivity tensor equation (2.21b). We inserted a subscript $p$ to equations (2.21b), (2.22) and (2.23) to remind readers that the corresponding matrices have been specified in terms of the principal coordinate system of each ellipsoid. Let us now compute a new resistivity tensor for the tilted ellipsoid as:

$$\overleftrightarrow{\rho}_t^{(\nu)} = \overleftrightarrow{\mathfrak{B}}_\theta \cdot \overleftrightarrow{\rho}_p^{(\nu)} \cdot \overleftrightarrow{\mathfrak{B}}_\theta^T = \frac{1}{S_1^{(\nu)}e}\begin{bmatrix} 1/u_x^{(\nu)} & -Z_\nu H_z^{(\nu)}/c & Z_\nu H_y^{(\nu)}/c \\ Z_\nu H_z^{(\nu)}/c & 1/u_y^{(\nu)} & -Z_\nu H_x^{(\nu)}/c + 1/u \\ -Z_\nu H_y^{(\nu)}/c & Z_\nu H_x^{(\nu)}/c + 1/u & 1/u_z^{(\nu)} \end{bmatrix}, \tag{3.2a}$$

where the subscript $t$ refers to the expression that is found subsequent to the tilting operation. In the above, we have introduced the definitions:

$$\begin{aligned} 1/u_x^{(\nu)} &\equiv 1/u_{x'}^{(\nu)} & H_x^{(\nu)} &\equiv H_{x'}^{(\nu)} \\ 1/u_y^{(\nu)} &\equiv (\cos^2\theta)/u_{y'}^{(\nu)} + (\sin^2\theta)/u_{z'}^{(\nu)} & H_y^{(\nu)} &\equiv H_{y'}^{(\nu)}\cos\theta + H_{z'}^{(\nu)}\sin\theta \\ 1/u_z^{(\nu)} &\equiv (\cos^2\theta)/u_{z'}^{(\nu)} + (\sin^2\theta)/u_{y'}^{(\nu)} & H_z^{(\nu)} &\equiv -H_{y'}^{(\nu)}\sin\theta + H_{z'}^{(\nu)}\cos\theta \\ 1/u &\equiv \left(\frac{1}{u_{z'}^{(\nu)}} - \frac{1}{u_{y'}^{(\nu)}}\right)\sin\theta\cos\theta. \end{aligned} \tag{3.2b}$$

By straightforward inversion of equation (3.2a), one obtains the conductivity tensor associated with the $\nu^{\text{th}}$ tilted ellipsoid as:

$$\overleftrightarrow{\sigma}_t^{(\nu)} = \frac{S_1^{(\nu)}e}{D_\sigma^{(\nu)}}\begin{bmatrix} \frac{1}{u_y u_z} - \frac{1}{u^2} + \left(\frac{H_x^{(\nu)}}{c}\right)^2 & \frac{Z_\nu H_z^{(\nu)}}{u_z c} + \frac{Z_\nu H_y^{(\nu)}}{uc} + \frac{H_x^{(\nu)}H_y^{(\nu)}}{c^2} & \frac{-Z_\nu H_y^{(\nu)}}{u_y c} - \frac{Z_\nu H_z^{(\nu)}}{uc} + \frac{H_x^{(\nu)}H_z^{(\nu)}}{c^2} \\ \frac{-Z_\nu H_z^{(\nu)}}{u_z c} - \frac{Z_\nu H_y^{(\nu)}}{uc} + \frac{H_x^{(\nu)}H_y^{(\nu)}}{c^2} & \frac{1}{u_x u_z} + \left(\frac{H_y^{(\nu)}}{c}\right)^2 & \frac{Z_\nu H_x^{(\nu)}}{u_x c} - \frac{1}{u_x u} + \frac{H_y^{(\nu)}H_z^{(\nu)}}{c^2} \\ \frac{Z_\nu H_y^{(\nu)}}{u_y c} + \frac{Z_\nu H_z^{(\nu)}}{uc} + \frac{H_x^{(\nu)}H_y^{(\nu)}}{c^2} & \frac{-Z_\nu H_x^{(\nu)}}{u_x c} - \frac{1}{u_x u} + \frac{H_y^{(\nu)}H_z^{(\nu)}}{c^2} & \frac{1}{u_x u_y} + \left(\frac{H_z^{(\nu)}}{c}\right)^2 \end{bmatrix}, \tag{3.3a}$$

where

$$D_\sigma^{(\nu)} \equiv \Delta^{(\nu)}/u_x u_y u_z - (1/u)(1/u_x u - 2H_y^{(\nu)}H_z^{(\nu)}/c^2); \tag{3.3b}$$

and

$$\Delta^{(\nu)} \equiv 1 + u_y u_z(H_x^{(\nu)}/c)^2 + u_x u_z(H_y^{(\nu)}/c)^2 + u_x u_y(H_z^{(\nu)}/c)^2. \tag{3.3c}$$

According to the model adopted here, the tilting operation is unnecessary for ellipsoid $\nu = 4$ in the valence band; its appropriate conductivity tensor is given by equation (2.16). In principle, the various mobilities in equation (3.3) should be indexed with a superscript $\nu$ as well, but the latter is temporarily omitted for the sake of clarity.

The Seebeck tensor for the electrons, equation (2.22), which has been constructed subject to the assumption that the $\tau_{\lambda'}$ are independent of $\varepsilon$, is isotropic in the present approximation, and therefore remains unaffected by the tilting operation. Also, the electronic contribution to the thermal conductivity associated with the charge carriers in a particular ellipsoid can be obtained via equation (2.23).

Before summing the individual $\overleftrightarrow{\boldsymbol{\sigma}}_t^{(\nu)}$ into a total conductivity tensor, it is necessary to rotate ellipsoids $\nu = 2,3$ so that their principal axes coincide with those of the crystal axes (the ellipsoid $\nu = 1$ is already properly aligned). For this purpose, we introduce the transformations (rotations about the $z$ axis by 120° and 240°):

$$\overleftrightarrow{\mathfrak{B}}_{120} = \begin{bmatrix} -\frac{1}{2} & \sqrt{\frac{3}{2}} & 0 \\ -\sqrt{\frac{3}{2}} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \overleftrightarrow{\mathfrak{B}}_{240} = \begin{bmatrix} -\frac{1}{2} & -\sqrt{\frac{3}{2}} & 0 \\ \sqrt{\frac{3}{2}} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}. \tag{3.4}$$

Their effect is found by carrying out the similarity transformations $\overleftrightarrow{\boldsymbol{\sigma}}^{\binom{3}{2}} = \overleftrightarrow{\mathfrak{B}}_{\substack{240\\120}} : \overleftrightarrow{\boldsymbol{\sigma}}_t^{\binom{3}{2}} : \overleftrightarrow{\mathfrak{B}}_{\substack{120\\240}}$ on equation (3.3a). We then obtain:

$$\overleftrightarrow{\boldsymbol{\sigma}}^{\binom{3}{2}} = \frac{S_1 e}{D_\sigma^{\binom{3}{2}}} \begin{bmatrix} \begin{array}{l} \frac{3}{4}\frac{1}{u_x u_z} + \frac{1}{4}\frac{1}{u_y u_z} + \\ + \frac{H_x^2}{c^2} - \frac{1}{4}\frac{1}{u^2} \end{array} & \begin{array}{l} \pm\frac{\sqrt{3}}{4}\frac{1}{u_x u_z} \mp \frac{\sqrt{3}}{4}\frac{1}{u_y u_z} + \\ + \frac{Z_\nu}{u_z}\frac{H_z}{c} + \frac{H_x H_y}{c^2} \pm \\ \pm\frac{\sqrt{3}}{4}\frac{1}{u^2} + \frac{Z_\nu}{2u}\left(\mp\sqrt{3}\frac{H_x}{c} - \frac{H_y}{c}\right) \end{array} & \begin{array}{l} \mp\frac{\sqrt{3}}{4}\frac{Z_\nu}{u_x}\left(\frac{-H_x}{c} \pm \sqrt{3}\frac{H_y}{c}\right) + \\ + \frac{1}{4}\frac{Z_\nu}{u_y}\left(\mp\sqrt{3}\frac{H_x}{c} - \frac{H_y}{c}\right) + \\ + \frac{H_x H_z}{c^2} + \frac{Z_\nu}{2u}\frac{H_z}{c} \pm \frac{\sqrt{3}}{2}\frac{1}{u_x u} \end{array} \\[2em] \begin{array}{l} \pm\frac{\sqrt{3}}{4}\frac{1}{u_x u_z} \mp \frac{\sqrt{3}}{4}\frac{1}{u_y u_z} \\ \frac{-Z_\nu}{u_z}\frac{H_z}{c} + \frac{H_x H_y}{c^2} \pm \frac{\sqrt{3}}{4}\frac{1}{u^2} - \\ \frac{-Z_\nu}{2u}\left(\mp\sqrt{3}\frac{H_x}{c} - \frac{H_y}{c}\right) \end{array} & \begin{array}{c} \frac{1}{4u_x u_z} + \frac{3}{4}\frac{1}{u_y u_z} + \left(\frac{H_y}{c}\right)^2 - \\ -\frac{3}{4u^2} \end{array} & \begin{array}{l} -\frac{1}{4}\frac{Z_\nu}{u_x}\left(\frac{-H_x}{c} \pm \sqrt{3}\frac{H_y}{c}\right) \mp \\ \mp\frac{\sqrt{3}}{4}\frac{Z_\nu}{u_y}\left(\mp\sqrt{3}\frac{H_x}{c} - \frac{H_y}{c}\right) + \\ + \frac{H_y H_z}{c^2} \mp \frac{\sqrt{3}}{2}\frac{Z_\nu}{u}\frac{H_z}{c} + \frac{1}{2}\frac{1}{u u_x} \end{array} \\[2em] \begin{array}{l} \pm\frac{\sqrt{3}}{2}\frac{Z_\nu}{u_x}\left(\frac{-H_x}{c} \pm \sqrt{3}\frac{H_y}{c}\right) - \\ -\frac{1}{4}\frac{Z_\nu}{u_y}\left(\mp\sqrt{3}\frac{H_x}{c} - \frac{H_y}{c}\right) + \\ + \frac{H_x H_z}{c^2} \pm \frac{\sqrt{3}}{2}\frac{1}{u_x u} - \frac{1}{2}\frac{Z_\nu}{u}\frac{H_z}{c} \end{array} & \begin{array}{l} \frac{Z_\nu}{4u_x}\left(\frac{-H_x}{c} \pm \sqrt{3}\frac{H_y}{c}\right) \pm \\ \pm\frac{\sqrt{3}}{4}\frac{Z_\nu}{u_y}\left(\mp\sqrt{3}\frac{H_x}{c} - \frac{H_y}{c}\right) + \\ + \frac{H_y H_z}{c^2} \pm \frac{\sqrt{3}}{2}\frac{Z_\nu}{u}\frac{H_z}{c} + \frac{1}{2}\frac{1}{u_x u} \end{array} & \frac{1}{u_x u_y} + \left(\frac{H_z}{c}\right)^2 \end{bmatrix}, \tag{3.5a}$$

in which:

$$D_\sigma^{\binom{3}{2}} = \frac{1}{u_x u_y u_z}\left\{1 + \left(\pm\frac{\sqrt{3}}{2}\frac{H_y}{c} - \frac{1}{2}\frac{H_x}{c}\right)^2 u_y u_z + \left(\mp\frac{\sqrt{3}}{2}\frac{H_x}{c} - \frac{1}{2}\frac{H_y}{c}\right)^2 u_x u_z + \right.$$
$$\left. + \left(\frac{H_z}{c}\right)^2 u_x u_y\right\} - \frac{1}{u_x u^2} + \frac{2H_z}{uc}\left(\mp\frac{\sqrt{3}}{2}\frac{H_x}{c} - \frac{1}{2}\frac{H_y}{c}\right). \tag{3.5b}$$

In the above, we have also transformed the magnetic field components which were originally expressed in terms of the principal coordinate system of the tilted ellipsoids. The magnetic field with components $H_\lambda (\lambda = x, y, z)$ is now specified in the common coordinate system introduced earlier. In carrying out the transformation, use has been made of the relationships

$$H_x^{(\frac{3}{2})} = -\frac{1}{2}H_x \pm \frac{\sqrt{3}}{2}H_y, \quad H_y^{(\frac{3}{2})} = \mp\frac{\sqrt{3}}{2}H_x - \frac{1}{2}H_y, \quad H_z^{(\frac{3}{2})} = H_z;$$

one should also note that $H_\lambda^{(4)} \equiv H_\lambda^{(1)} \equiv H_\lambda (\lambda = x, y, z)$.

In principle, we are now in a position to obtain the total $\overleftrightarrow{\boldsymbol{\sigma}}$ tensor via equation (2.27). In practice, due to the denominators which differ for various $v$, the requisite algebraic manipulations become excessive; we must resort to an examination of special cases in order to obtain tractable results.

## 4. TRANSPORT TENSORS FOR BISMUTH WITH $\mathbf{H} = \hat{\mathbf{k}}H_z$

In this section, we specialize to the case where the magnetic field is aligned with the $z$ axis of the crystal coordinate system. With this specialization, the subsequent mathematical operations are considerably reduced.

We first demonstrate that for the conduction band, the transport integral $S_1^{(v)}$ may be replaced with $n_e/3$, where $n_e$ is the charge carrier density in the conduction band. This identity may be established by setting $n = 1$ in equation (2.13), introducing the changes in variable $x \equiv \varepsilon/kT$, $\eta_B \equiv \mu_B/kT$, and integrating by parts; one thus obtains:

$$S_1^{(v)} = 4\pi\sqrt{m_{x'}m_{y'}m_{z'}}(2kT/h^2)^{3/2}F_{1/2}(\eta_B) = n^{(v)}. \tag{4.1}$$

The central expression will be recognized as the density of charge carriers in a valley, $n^{(v)}$. Since we assume that there are three equivalent ellipsoids in the conduction band, it follows that $S_1^{(v)} = n_e/3$, as was to be proved.

In now adding the partial conductivities, we return to equation (3.3) for ellipsoid 1, to equation (3.5) for ellipsoids 2 and 3, and to equation (2.16) for ellipsoid 4. In these tensors, we set $H_x = H_y = 0$. Next, we restrict ourselves to the case where $n_e = n_h = n$, which applies to pure bismuth. Because of the considerable overlap between the valence and conduction bands, this equality is almost always experimentally encountered. Finally, we utilize the fact that $u_x^{(n)} \gg u_y^{(n)}$ and $u_x^{(p)} = u_y^{(p)}$, as has been experimentally well documented [5, 16].

For later use, we now construct, subject to the restrictions mentioned above, the partial conductivities of carriers in the two bands. These quantities are given by [see also equation (2.27)]:

$$\overleftrightarrow{\boldsymbol{\sigma}}_z^{(e)} = \sum_{v=1}^{3} \overleftrightarrow{\boldsymbol{\sigma}}_z^{(v)} \quad \text{and} \quad \overleftrightarrow{\boldsymbol{\sigma}}_z^{(h)} = \overleftrightarrow{\boldsymbol{\sigma}}_z^{(4)}.$$

The requisite algebraic manipulations are straightforward, though rather tedious, and lead to the following results:

$$\overleftrightarrow{\boldsymbol{\sigma}}_z^{(e)} = \frac{ne}{D_z}\begin{bmatrix} Au_x^{(n)}/2 & -(H_z/c)u_x^{(n)}u_y^{(n)} & 0 \\ (H_z/c)u_x^{(n)}u_y^{(n)} & Au_x^{(n)}/2 & 0 \\ 0 & 0 & u_z^{(n)}[1 + u_x^{(n)}u_y^{(n)}H_z^2/c^2] \end{bmatrix}, \tag{4.2a}$$

with

$$D_z \equiv A + u_x^{(n)}u_y^{(n)}H_z^2/c^2, \tag{4.2b}$$

and

$$A \equiv 1 - u_y^{(n)} u_z^{(n)} / u^{(n)2}. \tag{4.2c}$$

The corresponding tensor for holes is given by:

$$\overleftrightarrow{\sigma}_z^{(h)}(H_z) = \frac{ne}{\Delta_z} \begin{bmatrix} u_x^{(p)} & (H_z/c) u_x^{(p)2} & 0 \\ -(H_z/c) u_x^{(p)2} & u_x^{(p)} & 0 \\ 0 & 0 & u_z^{(p)} \Delta_z \end{bmatrix}, \tag{4.3a}$$

with

$$\Delta_z \equiv 1 + u_x^{(p)2} H_z^2 / c^2. \tag{4.3b}$$

From the above, one can then construct the total conductivity tensor as:

$$\overleftrightarrow{\sigma}_z(H_z) = \frac{ne}{D_z \Delta_z} \begin{bmatrix} A\Delta_z u_x^{(n)}/2 + D_z u_x^{(p)} & -(H_z/c)[\Delta_z u_x^{(n)} u_y^{(n)} - D_z u_x^{(p)2}] & 0 \\ (H_z/c)[\Delta_z u_x^{(n)} u_y^{(n)} - D_z u_x^{(p)2}] & A\Delta_z u_x^{(n)}/2 + D_z u_x^{(p)} & 0 \\ 0 & 0 & \Delta_z u_z^{(n)} \left[1 + \dfrac{u_x^{(n)} u_y^{(n)} H_z^2}{c^2}\right] + \Delta_z D_z u_z^{(p)} \end{bmatrix}. \tag{4.4}$$

The resistivity tensor is thus given by:

$$\overleftrightarrow{\rho}_z \equiv \overleftrightarrow{\sigma}_z^{-1} = \frac{D_z \Delta_z}{ne D_z''} \begin{bmatrix} A\Delta_z u_x^{(n)}/2 + D_z u_x^{(p)} & (H_z/c)[\Delta_z u_x^{(n)} u_y^{(n)} - D_z u_x^{(p)2}] & 0 \\ -(H_z/c)[\Delta_z u_x^{(n)} u_y^{(n)} - D_z u_x^{(p)2}] & A\Delta_z u_x^{(n)}/2 + D_z u_x^{(p)} & 0 \\ 0 & 0 & (D_z'')^2/D_z' \end{bmatrix}, \tag{4.5a}$$

in which:

$$D_z' = \Delta_z \{ u_z^{(n)} [1 + u_x^{(n)} u_y^{(n)} H_z^2 / c^2] + D_z u_z^{(p)} \} D_z''; \tag{4.5b}$$

and

$$D_z'' = [A\Delta_z u_x^{(n)}/2 + D_z u_x^{(p)}]^2 + [(H_z/c)(\Delta_z u_x^{(n)} u_y^{(n)} - D_z u_x^{(p)2})]^2. \tag{4.5c}$$

The generalized Seebeck tensor may now be determined according to the relation $\overleftrightarrow{\mathfrak{p}}_z = \overleftrightarrow{\rho}_z : (\overleftrightarrow{\sigma}_z^{(e)} : \overleftrightarrow{\mathfrak{p}}_e + \overleftrightarrow{\sigma}_z^{(h)} : \overleftrightarrow{\mathfrak{p}}_h)$, which is a reformulation of equation (2.28) as applied to the present case. The partial conductivity tensors are given by equations (4.2) and (4.3), the total resistivity tensor, by equation (4.4), and the quantities $\overleftrightarrow{\mathfrak{p}}_{e,h} \equiv \mathfrak{p}_{e,h}[\![1]\!]$ are specified by equation (2.22). On carrying out the indicated operations, one obtains:

$$\overleftrightarrow{\mathfrak{p}}_z(H_z) = \frac{1}{D_z''} \begin{bmatrix} \mathfrak{p}_{xx}(H_z) & \mathfrak{p}_{xy}(H_z) & 0 \\ \mathfrak{p}_{xy}(-H_z) & \mathfrak{p}_{xx}(H_z) & 0 \\ 0 & 0 & \mathfrak{p}_{zz}(H_z) \end{bmatrix}, \tag{4.6a}$$

where

$$\mathfrak{p}_{xx}(H_z) = [A\mathfrak{p}_e \Delta_z u_x^{(n)}/2 + \mathfrak{p}_h D_z u_x^{(p)}][A\Delta_z u_x^{(n)}/2 + D_z u_x^{(p)}] + \\ + (H_z/c)^2 [\mathfrak{p}_e \Delta_z u_x^{(n)} u_y^{(n)} - \mathfrak{p}_h D_z u_x^{(p)2}][\Delta_z u_x^{(n)} u_y^{(n)} - D_z u_x^{(p)2}]; \tag{4.6b}$$

$$\mathfrak{p}_{xy}(H_z) = (H_z/c)\{[A\mathfrak{p}_e\Delta_z u_x^{(n)}/2 + \mathfrak{p}_h D_z u_x^{(p)}][\Delta_z u_x^{(n)} u_y^{(n)} - D_z u_x^{(p)^2}] -$$

$$- [A\Delta_z u_x^{(n)}/2 + D_z u_x^{(p)}][\mathfrak{p}_e\Delta_z u_x^{(n)} u_y^{(n)} - \mathfrak{p}_h D_z u_x^{(p)^2}]\}; \qquad (4.6c)$$

$$\mathfrak{p}_{zz}(H_z) = (D_z''/D_z')\{\mathfrak{p}_e\Delta_z u_z^{(n)}[1 + u_x^{(n)} u_y^{(n)} H_z^2/c^2] + \mathfrak{p}_h D_z \Delta_z u_z^{(p)}\}. \qquad (4.6d)$$

The above results are too cumbersome to be of use in the calculations. Accordingly, we consider two limiting cases, (a) $(u_\lambda^{(b)} H_\nu/c)^2 \ll 1$ ("weak field case"), and (b) $(u_\lambda^{(b)} H_\nu/c)^2 \gg 1$ ("strong field case") where $\lambda, \nu = x, y, z$ and $b = n, p$. One should remember that in the latter case, all quantum oscillatory phenomena are left out of account, so that the strong field results should be regarded as approximations to the region of intermediate field strengths where quantum effects are not yet appreciable.

A limiting process in which terms of order $H_z^2$ or higher are neglected leads to the results shown below:

$$\lim_{H_z \to 0} \overleftrightarrow{\rho}_z = \frac{1}{Ane(u_x^{(n)}/2 + u_x^{(p)})^2} \begin{bmatrix} A(u_x^{(n)}/2 + u_x^{(p)}) & (H_z/c)(u_x^{(n)} u_y^{(n)} - Au_x^{(p)^2}) & 0 \\ -(H_z/c)(u_x^{(n)} u_y^{(n)} - Au_x^{(p)^2}) & A(u_x^{(n)}/2 + u_x^{(p)}) & 0 \\ 0 & 0 & \dfrac{A^2(u_x^{(n)}/2 + u_x^{(p)})^2}{u_z^{(n)} + Au_z^{(p)}} \end{bmatrix}; \qquad (4.7)$$

$$\lim_{H_z \to 0} \overleftrightarrow{\mathfrak{p}}_z = \frac{1}{A^2(u_x^{(n)}/2 + u_x^{(p)})^2} \times$$

$$\times \begin{bmatrix} A^2(\mathfrak{p}_e u_x^{(n)}/2 + \mathfrak{p}_h u_x^{(p)})(u_x^{(n)}/2 + u_x^{(p)}) & \begin{matrix} -(H_z/c)Au_x^{(n)} u_x^{(p)}(\mathfrak{p}_e - \mathfrak{p}_h) \times \\ \times (u_y^{(n)} + Au_x^{(p)}/2) \end{matrix} & 0 \\ \begin{matrix} (H_z/c)Au_x^{(n)} u_x^{(p)}(\mathfrak{p}_e - \mathfrak{p}_h) \times \\ \times (u_y^{(n)} + Au_x^{(p)}/2) \end{matrix} & A^2(\mathfrak{p}_e u_x^{(n)}/2 + \mathfrak{p}_h u_x^{(p)})(u_x^{(n)}/2 + u_x^{(p)}) & 0 \\ 0 & 0 & \dfrac{A^2(u_x^{(n)}/2 + u_x^{(p)})^2(\mathfrak{p}_e u_z^{(n)} + \mathfrak{p}_h Au_z^{(p)})}{u_z^{(n)} + Au_z^{(p)}} \end{bmatrix}. \qquad (4.8)$$

Likewise, on retaining only the highest even and odd powered terms in (4.5) and (4.6), the strong field results read:

$$\lim_{H_z \to \infty} \overleftrightarrow{\rho}_z = \frac{1}{ne} \begin{bmatrix} \dfrac{2u_x^{(p)} u_y^{(n)}(H_z/c)^2}{Au_x^{(p)} + 2u_y^{(n)}} & \dfrac{4u_y^{(n)}(u_x^{(n)} u_y^{(n)} - Au_x^{(p)^2})(H_z/c)}{u_x^{(n)}(Au_x^{(p)} + 2u_y^{(n)})^2} & 0 \\ \dfrac{-4u_y^{(n)}(u_x^{(n)} u_y^{(n)} - Au_x^{(p)^2})(H_z/c)}{u_x^{(n)}(Au_x^{(p)} + 2u_y^{(n)})^2} & \dfrac{2u_x^{(p)} u_y^{(n)}(H_z/c)^2}{Au_x^{(p)} + 2u_y^{(n)}} & 0 \\ 0 & 0 & \dfrac{1}{u_z^{(n)} + u_z^{(p)}} \end{bmatrix}; \qquad (4.9)$$

$$\lim_{H_z \to \infty} \overleftrightarrow{\mathfrak{p}}_z = \begin{bmatrix} \dfrac{4u_y^{(n)}(u_x^{(n)} u_y^{(n)} - Au_x^{(p)^2})(\mathfrak{p}_e - \mathfrak{p}_h)}{u_x^{(n)}(Au_x^{(p)} + 2u_y^{(n)})^2} & \dfrac{-2u_x^{(p)} u_y^{(n)}(\mathfrak{p}_e - \mathfrak{p}_h)(H_z/c)}{Au_x^{(p)} + 2u_y^{(n)}} & 0 \\ \dfrac{2u_x^{(p)} u_y^{(n)}(\mathfrak{p}_e - \mathfrak{p}_h)(H_z/c)}{Au_x^{(p)} + 2u_y^{(n)}} & \dfrac{4u_y^{(n)}(u_x^{(n)} u_y^{(n)} - Au_x^{(p)^2})(\mathfrak{p}_e - \mathfrak{p}_h)}{u_x^{(n)}(Au_x^{(p)} + 2u_y^{(n)})^2} & 0 \\ 0 & 0 & \dfrac{\mathfrak{p}_e u_z^{(n)} + \mathfrak{p}_h u_z^{(p)}}{u_z^{(n)} + u_z^{(p)}} \end{bmatrix}. \qquad (4.10)$$

Attention is directed to the fact that one must proceed via the exact tensor, equation (4.5), before taking the limit $H_z \to \infty$ because in several instances the leading term of the high field approximation vanishes identically. In these situations, the corresponding entries involve terms of the next lower order in $H_z$.

A discussion of the above results is deferred to Part II of this paper.

## 5. TRANSPORT TENSORS FOR BISMUTH FOR $\mathbf{H} = \hat{\imath}H_x$ AND $\mathbf{H} = \hat{\jmath}H_y$

Two other cases which remain relatively tractable are those for which the magnetic field points along the $x$ or $y$ directions of the crystal system. The procedure is exactly the same as outlined in Section 4 and reviewed again in Section 6, except that different magnetic field components are set equal to zero. We shall therefore only cite the final results. Despite all the simplifications used so far, the analogues of equations (4.5) and (4.6) for the quantities $\overleftrightarrow{\boldsymbol{\rho}}_x$, $\overleftrightarrow{\mathbf{p}}_x$, $\overleftrightarrow{\boldsymbol{\rho}}_y$, $\overleftrightarrow{\mathbf{p}}_y$ are extremely cumbersome; there seems little point in setting them down. Instead, we proceed directly to the weak and strong field limits cited below. We find:

$$\lim_{H_x \to 0} \overleftrightarrow{\boldsymbol{\rho}}_x = \frac{1}{neD^0}\begin{bmatrix} 2(u_z^{(n)} + Au_z^{(p)}) & 0 & 0 \\ 0 & 2(u_z^{(n)} + Au_z^{(p)}) & (u_x^{(n)}u_z^{(n)} - 2Au_x^{(p)}u_z^{(p)})H_x/c \\ 0 & -(u_x^{(n)}u_z^{(n)} - 2Au_x^{(p)}u_z^{(p)})H_x/c & A(u_x^{(n)} + 2u_x^{(p)}) \end{bmatrix}, \tag{5.1a}$$

with

$$D^0 \equiv (u_x^{(n)} + 2u_x^{(p)})(u_z^{(n)} + Au_z^{(p)}); \tag{5.1b}$$

and

$$\lim_{H_x \to \infty} \overleftrightarrow{\boldsymbol{\rho}}_x = \frac{1}{neD^\infty}\begin{bmatrix} \dfrac{3D^\infty}{u_x^{(n)} + 3u_x^{(p)}} & 0 & 0 \\ 0 & u_z^{(n)}u_z^{(p)}(3u_y^{(n)} + u_x^{(p)})(H_x/c)^2 & \begin{matrix}(H_x/c)(3u_y^{(n)}u_z^{(n)} - Au_x^{(p)}u_z^{(p)}) + \\ +(H_x/c)^2 u_y^{(n)}u_z^{(n)}u_x^{(p)}u_z^{(p)}/u^{(n)}\end{matrix} \\ 0 & \begin{matrix}-(H_x/c)(3u_y^{(n)}u_z^{(n)} - Au_x^{(p)}u_z^{(p)}) + \\ +(H_x/c)^2 u_y^{(n)}u_z^{(n)}u_x^{(p)}u_z^{(p)}/u^{(n)}\end{matrix} & u_y^{(n)}u_x^{(p)}[(2A+1)u_z^{(p)} + 3u_z^{(n)}](H_x/c)^2 \end{bmatrix}. \tag{5.2a}$$

with

$$D^\infty \equiv (3u_y^{(n)} + u_x^{(p)})(u_z^{(n)} + u_z^{(p)}) - (u_y^{(n)}u_z^{(n)}u_z^{(p)}/u^{(n)2})(2u_y^{(n)} + u_x^{(p)}); \tag{5.2b}$$

$$\lim_{H_y \to 0} \overleftrightarrow{\boldsymbol{\rho}}_y = \frac{1}{neD^0}\begin{bmatrix} 2(u_z^{(n)} + Au_z^{(p)}) & 0 & -(H_y/c)[2Au_x^{(p)}u_z^{(p)} - u_x^{(n)}u_z^{(n)}] \\ 0 & 2(u_z^{(n)} + Au_z^{(p)}) & 0 \\ (H_y/c)[2Au_x^{(p)}u_z^{(p)} - u_x^{(n)}u_z^{(n)}] & 0 & A(u_x^{(n)} + 2u_x^{(p)}) \end{bmatrix}; \tag{5.3}$$

$$\lim_{H_y\to\infty}\overleftrightarrow{\rho}_y=\frac{1}{neD^{\infty}}\begin{bmatrix} u_z^{(n)}u_z^{(p)}(3u_y^{(n)}+u_x^{(p)})(H_y/c)^2 & -(H_y/c)u_y^{(n)}u_z^{(n)}u_z^{(p)}/u^{(n)} & \begin{array}{l}(H_y/c)[u_y^{(n)}u_x^{(p)}u_z^{(p)}(1-A)-\\ -(u_x^{(p)}+3u_y^{(n)})(u_x^{(n)}u_z^{(n)}-\\ \dfrac{-3Au_x^{(p)}u_z^{(p)})]}{u_x^{(n)}+3u_x^{(p)}}\end{array} \\ (H_y/c)u_y^{(n)}u_z^{(n)}u_z^{(p)}/u^{(n)} & Au_z^{(p)}+u_z^{(n)} & \begin{array}{l}2u_x^{(p)}u_z^{(p)}u_y^{(n)}A-\\ \dfrac{-u_y^{(n)}u_z^{(n)}(u_x^{(n)}+u_x^{(p)})}{u^{(n)}(u_x^{(n)}+3u_x^{(p)})}\end{array} \\ \begin{array}{l}-(H_y/c)[u_y^{(n)}u_x^{(p)}u_z^{(p)}(1-A)-\\ -(u_x^{(p)}+3u_y^{(n)})(u_x^{(n)}u_z^{(n)}-\\ \dfrac{-3Au_x^{(p)}u_z^{(p)})]}{u_x^{(n)}+3u_x^{(p)}}\end{array} & \begin{array}{l}[2Au_x^{(p)}u_z^{(p)}u_y^{(n)}-\\ \dfrac{-u_y^{(n)}u_z^{(n)}(u_x^{(p)}+u_x^{(n)})]}{u^{(n)}(u_x^{(n)}+3u_x^{(p)})}\end{array} & \dfrac{u_x^{(n)}u_x^{(p)}(H_y/c)^2D^{\infty}}{(u_x^{(n)}+3u_x^{(p)})} \end{bmatrix}. \tag{5.4}$$

This disposes of the various resistivities. The Seebeck–Nernst tensors in these approximations are given by:

$$\lim_{H_x\to 0}\overleftrightarrow{\mathfrak{p}}_x=\frac{1}{D^{0}}\begin{bmatrix} (u_z^{(n)}+Au_z^{(p)})(\mathfrak{p}_e u_x^{(n)}+2\mathfrak{p}_h u_x^{(p)}) & 0 & 0 \\ 0 & (u_z^{(n)}+Au_z^{(p)})(\mathfrak{p}_e u_x^{(n)}+2\mathfrak{p}_h u_x^{(p)}) & -u_z^{(n)}u_z^{(p)}(u_x^{(n)}+2u_x^{(p)})(\mathfrak{p}_e-\mathfrak{p}_h)H_x/c \\ 0 & u_x^{(n)}u_x^{(p)}(u_z^{(n)}+Au_z^{(p)})(\mathfrak{p}_e-\mathfrak{p}_h)H_x/c & (u_x^{(n)}+2u_x^{(p)})(\mathfrak{p}_e u_z^{(n)}+A\mathfrak{p}_h u_z^{(p)}) \end{bmatrix}; \tag{5.5}$$

$$\lim_{H_x\to\infty}\overleftrightarrow{\mathfrak{p}}_x=\frac{1}{D^{\infty}}\begin{bmatrix} \dfrac{[\mathfrak{p}_e u_x^{(n)}+3\mathfrak{p}_h u_x^{(p)}]D^{\infty}}{u_x^{(n)}+3u_x^{(p)}} & 0 & 0 \\ 0 & \begin{array}{l}\mathfrak{p}_e u_z^{(p)}[Au_x^{(p)}+(2A+1)u_y^{(n)}]+\\ +\mathfrak{p}_h u_z^{(n)}(3u_y^{(n)}+u_x^{(p)})+\\ +(H_x/c)(\mathfrak{p}_e-\mathfrak{p}_h)u_y^{(n)}u_z^{(n)}u_x^{(p)}u_z^{(p)}/u^{(n)}\end{array} & \begin{array}{l}-(\mathfrak{p}_e-\mathfrak{p}_h)u_z^{(n)}u_z^{(p)}\{u_y^{(n)}/u^{(n)}+\\ +(H_x/c)(u_x^{(p)}+3u_y^{(n)})\}\end{array} \\ 0 & \begin{array}{l}-(\mathfrak{p}_e-\mathfrak{p}_h)u_y^{(n)}u_x^{(p)}\{u_z^{(n)}/u^{(n)}\\ -(H_x/c)[3u_z^{(n)}+(2A+1)u_z^{(p)}]\}\end{array} & \begin{array}{l}\mathfrak{p}_e u_x^{(p)}(u_z^{(n)}+Au_z^{(p)})+\mathfrak{p}_h u_y^{(n)}[3u_z^{(n)}+\\ +(2A+1)u_z^{(p)}]-\\ -(\mathfrak{p}_e-\mathfrak{p}_h)(u_y^{(n)}u_z^{(n)}u_x^{(p)}u_z^{(p)}/u^{(n)})(H_x/c)\end{array} \end{bmatrix}; \tag{5.6}$$

$$\lim_{H_y\to 0}\overleftrightarrow{\mathfrak{p}}_y=\frac{1}{D^{0}}\begin{bmatrix} (u_z^{(n)}+Au_z^{(p)})(\mathfrak{p}_e u_x^{(n)}+2\mathfrak{p}_h u_x^{(p)}) & 0 & \begin{array}{l}u_z^{(n)}u_z^{(p)}(u_x^{(n)}+2u_x^{(p)})\times\\ \times(\mathfrak{p}_e-\mathfrak{p}_h)H_y/c\end{array} \\ 0 & (u_z^{(n)}+Au_z^{(p)})(\mathfrak{p}_e u_x^{(n)}+2\mathfrak{p}_h u_x^{(p)}) & 0 \\ -u_x^{(n)}u_x^{(p)}(u_z^{(n)}+Au_z^{(p)})(\mathfrak{p}_e-\mathfrak{p}_h)H_y/c & 0 & \begin{array}{l}(u_x^{(n)}+2u_x^{(p)})(\mathfrak{p}_e u_z^{(n)}+\\ +A\mathfrak{p}_h u_z^{(p)})\end{array} \end{bmatrix}; \tag{5.7}$$

$$\lim_{H_y\to\infty} \overleftrightarrow{\mathfrak{p}}_y = \frac{1}{D^{\infty}}\begin{bmatrix} \dfrac{\begin{array}{l}\{u_z^{(n)}(u_x^{(p)}+3u_y^{(n)})(3\mathfrak{p}_e u_x^{(p)}+\mathfrak{p}_h u_x^{(n)}) \\ +\,u_z^{(p)}[\mathfrak{p}_e u_x^{(n)}(Au_x^{(p)}+2Au_y^{(n)}+u_y^{(n)})+ \\ +\,\mathfrak{p}_h u_x^{(p)}[(8A+1)u_y^{(n)}+3Au_x^{(p)}]]\}\end{array}}{u_x^{(n)}+3u_x^{(p)}} & \dfrac{u_y^{(n)}u_z^{(n)}u_x^{(p)}u_z^{(p)}(\mathfrak{p}_e-\mathfrak{p}_h)(H_y/c)}{u^{(n)}} & \begin{array}{l} u_z^{(n)}u_z^{(p)}(3u_y^{(n)}+u_x^{(p)})\times \\ \times(\mathfrak{p}_e-\mathfrak{p}_h)(H_y/c)\end{array} \\ \dfrac{-2u_y^{(n)}u_x^{(p)}(u_z^{(n)}+Au_z^{(p)})(\mathfrak{p}_e-\mathfrak{p}_h)}{(H_y/c)u^{(n)}(u_x^{(n)}+3u_x^{(p)})} & \begin{array}{l}\mathfrak{p}_e u_y^{(n)}u_z^{(p)}(1-A)+(Au_z^{(p)}+u_z^{(n)})\times \\ \times(3\mathfrak{p}_e u_y^{(n)}+\mathfrak{p}_h u_x^{(p)})\end{array} & \dfrac{u_z^{(p)}u_z^{(n)}u_y^{(n)}(\mathfrak{p}_e-\mathfrak{p}_h)}{u^{(n)}} \\ \dfrac{-u_x^{(n)}u_x^{(p)}(\mathfrak{p}_e-\mathfrak{p}_h)(H_y/c)D^{\infty}}{(u_x^{(n)}+3u_x^{(p)})} & \dfrac{\begin{array}{l}\{-u_y^{(n)}u_x^{(p)}(\mathfrak{p}_e-\mathfrak{p}_h)(2Au_x^{(p)}u_z^{(p)} \\ -\,u_x^{(n)}u_z^{(n)}-u_x^{(p)}u_z^{(n)})\}\end{array}}{(3u_x^{(p)}+u_x^{(n)})u^{(n)}} & \dfrac{\begin{array}{l}\{(3u_y^{(n)}+u_x^{(p)})(3u_x^{(p)}+u_x^{(n)})\times \\ \times(\mathfrak{p}_e u_z^{(n)}+\mathfrak{p}_h Au_z^{(p)}) \\ +\,u_y^{(n)}u_z^{(p)}(1-A)[2\mathfrak{p}_e u_x^{(p)} \\ +\,\mathfrak{p}_h(u_x^{(n)}+u_x^{(p)})]\}\end{array}}{(u_x^{(n)}+3u_x^{(p)})} \end{bmatrix}. \quad (5.8)$$

## 6. PRELIMINARY DISCUSSION

The above derivations provide all the results needed in the derivation of appropriate figures of merit for Bi; this extension of the work and the comparison between theory and experiment is deferred to Part II of this paper. However, at this stage it is worthwhile to review in outline form the general procedure and assumptions used in the derivations so far.

Starting with the conventional formulation of the electric and thermal currents in terms of transport integrals, the distribution function was determined by solving the Boltzmann transport equation in the relaxation time formalism. Allowance was made for anisotropy of the medium and for the joint action of electric, magnetic, and temperature fields. The results so obtained specify the fluxes $\mathbf{J}$ and $\mathbf{J}_Q$ in terms of the "forces" $\nabla(J/e)$ and $\nabla T$; after converting from $\mathbf{J}_Q$ to $\mathbf{J}_S$ one obtains a set of phenomenological equations satisfying the Casimir–Onsager reciprocity conditions. On partial inversion of these relations, whereby $\nabla(J/e)$ and $\mathbf{J}_S$ were assigned the status of dependent variables, the phenomenological equations were cast in a form that permitted the identification of the resistivity, Seebeck, and thermal conductivity tensors in terms of transport integrals. Expressions so obtained were then properly summed to take into account the contributions arising from carriers in various conduction and valence band ellipsoids, allowance being made for the tilt of the former set about their respective binary axes.

The final results are based on the following simplifying assumptions: (a) $\varepsilon$ is assumed to vary quadratically with the wave number vector components, (b) only contributions due to the overlapping valence and conduction bands were considered, (c) the relaxation time formalism was used in solving the Boltzmann equation, (d) all phonon-charge carrier interactions were presumed to be accounted for in specifying the relaxation time, and intervalley scattering effects were ignored, (e) hot electron effects and quantum effects in the high magnetic field region were not included. To obtain tractable analytic expressions, we also (f) considered only the special case in which the magnetic field is aligned with each of the crystal symmetry axes, (g) neglected, where permissible, $1/u_x^{(n)}$

relative to $1/u_y^{(n)}$ and set $u_x^{(p)} = u_y^{(p)}$, where the $u^{(b)}$ are electron or hole mobilities for $H = 0$ along the indicated crystal symmetry axes, ($h$) restricted ourselves to the intrinsic case by setting $n = p$, and (i) specialized to the case of low and high magnetic fields. Finally, (j) for the weak field limiting case, only terms of order $H^0$ and $H^1$ were retained.

## REFERENCES


[1] B. J. O'Brien and C. S. Wallace, *J. appl. Phys.* **29**, 1010 (1958).
[2] K. F. Cuff, R. B. Horst, J. L. Weaver, S. R. Hawkins, C. F. Kooi and G. M. Enslow, *Appl. Phys. Lett.* **2**, 145 (1963).
[3] C. F. Kooi, R. B. Horst, K. F. Cuff and S. R. Hawkins, *J. appl. Phys.* **34**, 1735 (1963).
[4] T. C. Harman, J. M. Honig, S. Fischler, A. E. Paladino and M. Jane Button, *Appl. Phys. Lett.* **4**, 77 (1964); Paper 842A *Amer. Soc. mech. Engrs.*
[5] B. Abeles and S. Meiboom, *Phys. Rev.* **101**, 544 (1956).
[6] R. B. Horst, *J. appl. Phys.* **34**, 3247 (1963).
[7] H. Jones, *Proc. roy. Soc.* **A147**, 396 (1934); **A155**, 653 (1936). D. Shoenberg, *Proc. roy. Soc.* **A170**, 341 (1939); *Trans. roy. Soc.* **A245**, 1 (1952).
[8] T. C. Harman and J. M. Honig, *Semiconductor Prods.* **6**, 19 (1963).
[9] T. C. Harman and J. M. Honig, *J. Phys. Chem. Solids* **23**, 913 (1962).
[10] A. H. Wilson, *The Theory of Metals.* University Press, Cambridge, 1958.
[11] C. Herring and E. Vogt, *Phys. Rev.* **101**, 944 (1956).
[12] M. Shibuya, *Phys. Rev.* **95**, 1385 (1954).
[13] W. M. Bullis, Ph.D. Thesis, Massachusetts Institute of Technology, 1956.
[14] T. C. Harman, J. M. Honig and B. M. Tarmy, *J. appl. Phys.* **34**, 189 (1963); 2215 (1963); 2225 (1963).
[15] Ref. 9, equation (3.12) and note added in proof of — T. C. Harman, J. M. Honig and B. M. Tarmy, *J. Phys. Chem. Solids* **24**, 835 (1963).
[16] B. Lax, J. G. Mavroides, H. J. Zeiger and R. J. Keyes, *Phys. Rev. Lett.* **5**, 241 (1960).
[17] V. Heine, *Proc. phys. Soc. Lond.* **A69**, 513 (1956); N. B. Brandt, *Soviet Phys.-JETP* **11**, 975 (1960); I. N. Kalinkina and P. G. Strekov, *Soviet Phys.-JETP* **7**, 426 (1958); L. S. Lerner, *Phys. Rev.* **127**, 1480 (1962).


**Résumé**—On a appliqué au bismuth le formalisme du temps de relaxation; les résultats sont utilisés, dans la partie II, pour déterminer le facteur de mérite du bismuth dans les processus de conversion d'énergie. En utilisant, pour le bismuth, le modèle de Jones–Shoenberg, on dérive des expressions analytiques de la résistivité électrique, de la conductivité thermique, et des coefficients de Hall, de Seebeck et de Nernst. On résout l'équation de transport de Boltzmann donnant la fonction de distribution perturbée, en utilisant des temps de relaxation anisotropes. Le résultat est alors introduit dans les intégrales de transport représentant le courant électrique et le flux d'énergie, pour aboutir aux équations phénoménologiques valables pour chaque groupe de porteurs de charge associé à un ellipsoïde donné. On additionne les contributions de chaque groupe de porteurs, dans le système de coordonnées du cristal, pour obtenir les coefficients de transport mentionnés ci-dessus. Pour obtenir des expressions analytiques, il est nécessaire de considérer les cas particuliers où le champ magnétique est aligné avec chacun des trois axes de symétrie, et de passer à la limite des champs magnétiques très faibles ou très forts.

**Zusammenfassung**—Die Transport-Theorie, begründet auf dem Relaxationszeit-Formalismus wird auf Wismut angewendet. Diese Erbebnisse werden dann in Teil II benutz, um die Güteziffer von Bi bei Energicumwandlungs-Prozessen zu bestimmen. Unter Benutzung des Jones–Shoenberg-Models für Wismut werden analytische Ausdrücke für den spezifischen elektrischen Widerstand, die Wärmeleitfähigkeit und für die Hall-, Seebeck- und Nernst-Koeffizienten abgeleitet. Die Boltzmann'sche Transportgleichung wird gelöst für gestörte Verteilungsfunktionen unter Benutzung von anisotropen Relaxationszeiten. Dieses Resultat wird dann in die Transport-Integrale für den elektrischen Strom und den Energiefluss eingeführt, um phänomenologische Gleichungen für jede Art von Ladungsträgern zu erhalten, die mit einem gegebenen Ellipsoid verbunden sind. Die Beiträge jeder Gruppe von Ladungsträgern werden dann addiert in dem gemeinsamen Symmetrie-Koordinatensystem des Kristalls, um die oben erwähnten Transportkoeffizienten zu erhalten. Um analytische Ausdrücke zu erhalten, war es notwendig, die Sonderfälle durchzuarbeiten, in denen das Magnetfeld mit jeder der drei Symmetrie-Achsen übereinstimmt und überzugehen auf die Grenzfälle sehr niedriger oder sehr hoher Magnetfelder.